

UNCLASSIFIED

AD 407711

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



■ UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

RESEARCH ON PHASES CONTAINING TRANSITION METALS
AND NON-METALS

Gunnar Hägg

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

Technical Final Report

Contract No. AF 61(052)-40

Covering period 1 January 1958 - 31 December 1962

The research reported in this document has been sponsored in part by the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OAR through the European Office, Aerospace Research, United States Air Force.

Research on phases containing transition metals
and non-metals

This report deals with accurate determinations of basic properties of phases in systems of transition metals and non-metals. These studies are mainly confined to the borides, silicides and phosphides of transition metals from Groups VI, VII and VIII. Comprehensive and detailed reviews of the binary transition metal borides, silicides and phosphides have been given in Technical Notes No. 13 and 34. The present report is therefore confined to general aspects only, which are presented in two main paragraphs: "Phase analyses" and "Crystal chemistry". Some further comments are made on very recent results not included in the Technical Notes mentioned above.

Phase analyses

In spite of very intense basic research on binary transition metal borides, silicides and phosphides, the characterisation of these phases is in many cases incomplete. This is particularly true for phases containing rare earth metals, but also for phases containing e.g. Group IV and V transition metals. In many systems, the number and approximate composition of the phases may be known, but the lack of quantitative information about homogeneity ranges and melting points prevents the construction of the complete equilibrium diagrams.

Our phase-analytical work has been devoted to the solid regions of some 35 binary and 15 ternary systems. The alloys have been prepared by heating weighed amounts of the component elements at high temperatures under carefully controlled conditions. Special efforts have been made to ensure high purity and equilibrium conditions of the products. The X-ray powder diffraction technique and chemical analytical methods have been the chief research tools.

Borides. Binary borides of the following metals have been investigated: Cr, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. Detailed reports have been given in Technical Notes No. 1, 5, 6, 8, 11, 13, 16, 17, 20, 25 and 32. The phase relationships in the systems Cr-B, Mn-B, Re-B, Fe-B, Ru-B, Os-B, Co-B and Ni-B are fairly well clarified. However, the compositions of the boron-rich phases in the Re-B, Ru-B, Os-B (and also Mo-B and W-B¹) systems are still somewhat uncertain. It was first pointed out by La Placa and Post² that only a fraction of the available crystallographic positions for the boron atoms are occupied in the structure of the most boron-rich phase in the Re-B system, and similar results have recently been obtained by Roof and Kempter³ in the Ru-B and Os-B systems. Further studies seem desirable.

○ In re-investigations of binary boride systems, inconsistencies between the old and the more recent results have frequently been encountered. This is certainly in many cases caused by the high impurity content in the old boride preparations. For instance, heating metal and boron powder in evacuated and sealed silica tubes may lead to serious contamination of silicon and oxygen, and ternary boro-silicides may even be formed (see Technical Notes No. 2, 5, 6, 13 and 35). With the high-purity chemicals and good high-vacuum furnaces now available, much more accurate determinations of the Me-B phase diagrams can be made, which appears to be an important task for future research.

In recent studies the electrical properties of lanthanum boride have been investigated⁴. A number of investigations have been published on the mechanical properties of some borides, which may be useful as high-temperature construction materials⁵. In this connection a recent study of boron-containing titanium alloys may be mentioned⁶.

Few systematic studies of the chemical properties of borides seem to have been made. A better knowledge about oxidation of borides should be of great theoretical and practical interest.

Silicides. Binary silicides of the metals Mn, Fe, Ru, Co, Rh, Ni and Pd have been investigated as reported in Technical Notes No. 3, 5, 9, 15, 16, 18, 23 and 35. Although some recent studies⁷⁻¹³ have added to our knowledge of the silicides, a large number of Me-Si systems, in particular those containing platinum metals, are still very incompletely elucidated. However, as was mentioned in the case of borides, the experimental difficulties in determining the equilibrium diagrams are now largely overcome.

Some silicides have semi-conducting properties and high thermo-electric force, which has stimulated an intense research on these materials¹⁴⁻¹⁹. Few studies seem to have been devoted to the mechanical properties of silicides in "bulk form".

Phosphides. Binary phosphides of the following metals have been studied: Ti, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. The results have been reported in Technical Notes No. 2, 4, 7, 10, 12, 19, 21, 22, 24, 26, 28, 30, 31 and 33. The phase relationships have been well established in the solid regions of the systems Mo-P, W-P, Mn-P, Fe-P, Ru-P, Os-P, Co-P, Rh-P, Ir-P and Ni-P, while the conditions in the remaining systems need further clarification. In general, the homogeneity ranges for the phosphides investigated are very narrow. However, extended homogeneity ranges have been observed for some phases with the ideal composition Me_2P . Careful single-crystal investigations indicate that the extended homogeneity ranges can be interpreted in terms of metal atom vacancies in the structures (see Technical Notes No 12 and 30).

Recently, the occurrence of mono-phosphides of hafnium²⁰, scandium and yttrium²¹ has been demonstrated. However, the information regarding the phosphides of Groups III, IV and V transition metals is still rather scanty.

The physical properties of transition metal phosphides have hitherto been very little explored. Some data for mono-

phosphides of Ti, V, Nb, Ta, Cr, Mo, W and Mn were recently reported ²². All these phosphides are hard materials (comparable with hardened high-carbon steel) and resistivity measurements indicate metallic behaviour.

Ternary systems. A number of ternary systems containing transition metals and the non-metals boron, silicon and phosphorus have been investigated. In some cases more detailed studies have been made and phase-relationships and homogeneity ranges have been determined over large parts of the systems (the Fe-Si-B, Fe-P-B and Co-Si-B systems as reported in Technical Notes No. 3, 15, and 24). In other cases the work has been confined to explorations of selected smaller regions of the systems (the Mn-Si-B, Ni-Si-B, Cr-P-B, Mn-P-B, Co-P-B, Ni-P-B, Cr-Co-P, Mn-Co-P, Fe-Co-P, Fe-Si-P, Co-Si-P and Cr-Ni-P systems, reported in Technical Notes No. 2, 12, 15, 24, 26 and 28).

The interest has been largely devoted to systems containing one transition metal and two non-metals. The Me-Si-B and Me-P-B systems have many features in common, and several ternary isomorphous boro-silicides and boro-phosphides with the composition Me_5XB_2 occur. A notable feature is the large solubility of boron in the phosphides. The solubility of silicon and phosphorus in the borides is, however, very limited except in borides of the cementite type ($Fe_3(B, Si)$, Co_3B , Ni_3B). The behaviour of phosphorus and silicon in the stabilisation of sigma-phases has been found to be very similar (see Technical Note No. 26).

Crystal chemistry

The main effort in our work on transition metal borides, silicides and phosphides has been devoted to studies of the crystal chemistry of these compounds. Some 70 crystal structures have been determined. In most cases the single-crystal

technique has been employed, and interatomic distances and scattering parameters have been determined to a high degree of accuracy.

The results of these studies have been collected and discussed in a general way in Technical Notes No. 13, 29 and 34. The main observations are as follows.

The structural similarities between metal-rich borides, silicides and phosphides are pronounced. Isostructural compounds occur frequently, especially in systems containing Group VII and VIII transition metals. Boron and silicon substitute to a large extent for phosphorus in several phosphide structures, and isomorphous Si/P replacement has been observed in silicide structures. Several isomorphous ternary boro-phosphides and boro-silicides occur.

In correlating and classifying these structures, the size-factor concept has proved very useful. In particular, the ordered distribution of the non-metal atoms observed in the ternary boro-phosphide and boro-silicide structures is understandable from the size-factor point of view; the boron atoms occupy the smaller, and silicon and phosphorus atoms the larger voids in the metal lattices. Furthermore, it has been shown that simple geometrical and topological arguments can explain particular trends in interatomic distances observed in various series of isomorphous phases.

There are, however, notable structural features, which can hardly be explained in terms of the size-factor. In metal-rich phosphides there seems to be a tendency for the phosphorus atoms to avoid short P-P contacts. The near environment of the phosphorus atoms thus consists of metal atoms only. In silicide, and particularly in boride structures, short non-metal contacts occur frequently. The difference in this respect between phosphides on the one hand, and borides and silicides on the other becomes more pronounced in phases with high non-metal content, where the number of short P-P contacts is very restricted while short B-B and Si-Si contacts form infinite two- or three-dimensional networks in the structures.

The metal-non-metal distances are generally in close agreement with the sums of the Goldschmidt metal radii and the tetrahedral covalent radii for the non-metals. However, it has been found that when the group number of the transition metal increases there is a tendency for the formation of progressively shorter metal-non-metal distances in comparison with the above mentioned radius sums. Extremely short distances occur in phases containing nickel, palladium and platinum.

These examples illustrate the shortcomings of the size-factor concept and emphasize the need of a more fundamental approach in the structural discussion. Unfortunately, the present state of the chemical bond theories for compounds between transition metals and non-metals is very unsatisfactory (a brief résumé is given in Technical Note No. 13). The hypotheses put forward provide very little material for detailed structural discussions and are very far from giving an account of the various physical and chemical properties of the compounds. The task of formulating a quantitative theory of the chemical bond in these compounds is indeed formidable, and little success is expected in the near future. At present, it seems desirable to collect accurate data for the electric, magnetic, thermodynamic and other important physical properties. While such knowledge can be expected to lead to a better foundation for theoretical speculations, it would be invaluable in developing materials for future technical applications.

Conrad Häg

List of Technical Notes issued under Contract No AF 61(052)-40

1. The crystal structure of $\text{Ru}_{73}\text{B}_{27}$. B. Aronsson.
Acta Chem. Scand. 13, 109 (1959).
2. The structures of $\text{Ni}_6\text{Si}_2\text{B}$, Fe_2P and some related phases.
S. Rundqvist and F. Jellinek.
Acta Chem. Scand. 13, 425 (1959).
3. X-ray investigations on Me-Si-B systems (Me = Mn, Fe, Co).
I. Some features of the Co-Si-B system at 1000°C . Intermediate phases in the Co-Si-B and Fe-Si-B systems.
B. Aronsson and G. Lundgren
Acta Chem. Scand. 13, 433 (1959).
4. The crystal structure of Ni_{12}P_5 .
S. Rundqvist and E. Larsson.
Acta Chem. Scand. 13, 551 (1959).
5. Borides and silicides of the platinum metals.
B. Aronsson, J. Åselius and E. Stenberg
Nature 183, 1318 (1959).
6. An X-ray investigation of the nickel-boron system. The crystal structures of orthorhombic and monoclinic Ni_4B_3 .
S. Rundqvist
Acta Chem. Scand. 13, 1193 (1959).
7. Phosphides of the platinum metals.
S. Rundqvist
Nature 185, 31 (1960).
8. Borides of rhenium and the platinum metals.
B. Aronsson, J. Åselius and E. Stenberg.
Acta Chem. Scand. 14, 733 (1960).
9. The crystal structure of Pd_3Si .
B. Aronsson and A. Nylund
Acta Chem. Scand. 14, 1011 (1960).

10. X-ray investigation on rhodium phosphides. The crystal structure of Rh_4P_3 .
S. Rundqvist and A. Hede
Acta Chem. Scand. 14, 893 (1960).
11. The crystal structure of Re_3B .
B. Aronsson, M. Bäckman and S. Rundqvist.
Acta Chem. Scand. 14, 1001 (1960)
12. The structures of Co_2P , Ru_2P and related phases.
S. Rundqvist
Acta Chem. Scand. 14, 1961 (1960)
13. Borides and silicides of the transition metals.
B. Aronsson
Arkiv Kemi 16, 379 (1960)
14. Structural features of new phases with the cementite and related structures.
B. Aronsson and S. Rundqvist
Paper presented at the Fifth Int. Congr. of the Int. Union of Crystallography, Cambridge, 1960.
15. X-ray investigations on Me-Si-B systems (Me = Mn, Fe, Co).
II. Some features of the Fe-Si-B and Mn-Si-B systems.
B. Aronsson and I. Engström
Acta Chem. Scand. 14, 1403 (1960).
16. A note on the compositions and crystal structures of MnB_2 , Mn_3Si , Mn_5Si_3 and FeSi_2 .
B. Aronsson
Acta Chem. Scand. 14, 1414 (1960)
17. The crystal structure of Ru_{11}B_8 .
J. Åselius
Acta Chem. Scand. 14, 2169 (1960)
18. The crystal structure of Ni_3Si_2 with some notes on Ni_5Si_2 .
G. Pilström
Acta Chem. Scand. 15, 893 (1961)

19. The crystal structure of Re_2P .
S. Rundqvist
Acta Chem. Scand. 15, 342 (1961)
20. The crystal structures of Pd_5B_2 (Mn_5C_2) and Pd_3B .
E. Stenberg
Acta Chem. Scand. 15, 861 (1961).
21. The crystal structure of Pd_3P .
S. Rundqvist and L.-O. Gullmärt
Acta Chem. Scand. 14, 2246 (1960)
22. Diphosphides of the Group VIII transition metals.
S. Rundqvist
Acta Chem. Scand. 15, 451 (1961)
23. The crystal structure of Ru_2Si
B. Aronsson and J. Åselius
Acta Chem. Scand. 15, 1571 (1961)
24. X-ray investigations of the ternary system Fe-P-B. Some features of the systems Cr-P-B, Mn-P-B, Co-P-B and Ni-P-B.
S. Rundqvist
Acta Chem. Scand. 16, 1 (1962)
25. The crystal structure of Cr_3B_4 .
M. Elfström
Acta Chem. Scand. 15, 1178 (1961)
26. A ternary sigma phase in the system Cr-Ni-P.
T. Lundström
Acta Chem. Scand. 16, 149 (1962)
27. The crystal structures of two thorium germanide phases with compositions approximating to $\text{Th}_{0.9}\text{Ge}_2$ and ThGe_2 .
A. Brown
Acta Cryst. 15, 652 (1962)
28. Phosphides of the B 31 (MnP) structure type.
S. Rundqvist
Acta Chem. Scand. 16, 287 (1962)

29. Structural features of some phases related to cementite.
B. Aronsson and S. Rundqvist
Acta Cryst. 15, 878 (1962)
30. X-ray investigations of Mn_3P , Mn_2P and Ni_2P .
S. Rundqvist
Acta Chem. Scand. 16, 992 (1962)
31. Refinement of the Ni_3P structure.
S. Rundqvist, E. Hassler and L. Lundvik
Acta Chem. Scand. 16, 242 (1962)
32. Borides of ruthenium, osmium and iridium.
B. Aronsson, E. Stenberg and J. Åselius
Nature 195, 377 (1962)
33. X-ray studies of molybdenum and tungsten phosphides.
S. Rundqvist and T. Lundström
Acta Chem. Scand. in print.
34. Binary transition metal phosphides. Their structures and relationships with other compounds between transition metals and non-metals with small atomic radii.
S. Rundqvist
Arkiv Kemi 20, 67 (1962)
35. The crystal structures of Rh_2Si and Rh_5Si_3 with some notes on the Rh-Si system.
I. Engström
Acta Chem. Scand. in print.

References

1. New borides of molybdenum and tungsten, MoB_4 and WB_4 . A. Crétien and J. Helgorsky, Compt. rend. 252, 742 (1961).
2. Crystal structure of rhenium diboride. S. La Placa and B. Post, Acta Cryst. 15, 97 (1962).
3. New orthorhombic phase in Ru-B and Os-B systems. R.B. Roof Jr. and C.P. Kempfer, J. Chem. Phys. 37, 1473 (1962).
4. Electrical properties of lanthanum boride. G.V. Samsonov and V.S. Fomenko, Fiz. Metal. i Metalloved. 10, 633 (1960).
5. Selection and fabrication of ceramics and intermetallics. J.D. Latva, Met. Prop. 82, 139 (1962).
6. High-modulus titanium alloys containing boron and aluminium. A.R.G. Brown, H. Brooks, K.S. Jepson and G.I. Lewis, J. Inst. Metals 91, 161 (1962-63).
7. Phase components of the system MnSi-Si . V.A. Korshunov, F.A. Sidorenko, P.V. Gel'd and K.N. Davydov, Fiz. Metal. i Metalloved. 12, 277 (1961).
8. Martensite transformation in Mn_3Si . K.N. Davydov, F.A. Sidorenko and P.V. Gel'd. Fiz Metal. i Metalloved. 12, 424 (1961).
9. An X-ray investigation of the constitution of iron-rich iron-silicon alloys. F. Lihl and H. Ebel, Arch. Eisenhüttenw. 32, 489 (1961).
10. Polymorphism of rare-earth disilicides. J.A. Perry, E. Banks and B. Post, J. Phys. Chem. 63, 2073 (1959).
11. The crystal structures of Sc_5Si_3 , Sc_5Ge_3 and Ce_5Ge_3 . J. Arbuckle and E. Parthé, Acta Cryst. 15, 1205 (1962).
12. Rare-earth metal phase diagrams. C.E. Lundin in The rare earths, F.H. Spedding and A.H. Daane (ed.), John Wiley & Sons, Inc. New York and London, 1961.

13. The transformation of the ζ -phase in iron-silicon alloys. H. Holdhus, J. Iron Steel Inst. 200, 1024 (1962).
14. The use of high-temperature thermoelectric materials (silicides) for power generation in space. S.E. Mayer and I.M. Ritchie, Progress in Astronautics and Rocketry 3, 63 (1961).
15. Study of electrical conductivity of silicides of the transition metals. V.S. Neshpor and G.V. Samsonov, Fiz. Tverdogo Tela 2, 2202 (1960).
16. Thermoelectric properties of the chromium-silicon system. E.N. Nikitin, Fiz. Tverdogo Tela 2, 2685 (1960).
17. Rhenium disilicide as a new high-melting-point semiconductor. V.S. Neshpor and G.V. Samsonov, Fiz. Metal. i Metalloved. 11, 638 (1961).
18. The electrical properties of the higher silicide of manganese. V.A. Korshunov and P.V. Gél'd. Fiz. Metal. i Metalloved. 11, 945 (1961).
19. Chromium disilicide, its range of homogeneity and electrical properties. V.P. Trusova, V.S. Kutsev and B.F. Ormont. Zhur. Neorg. Khim. 5, 1119 (1960).
20. The structure of HfP. W. Jeitschko and H. Nowotny, Monatsh. 93, 1107 (1962).
21. Note on the structure of ScP and YP. E. Parthé and E. Parthé, Acta Cryst. 16, 71 (1963).
22. The preparation and properties of some transition phosphides. R.L. Ripley, J. Less-Common Metals 4, 496 (1962).